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Gasification characteristics of steam exploded biomass in an updraft pilot scale gasifier

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ABSTRACT

Pretreatment of biomass becomes more and more important due to the large scale application of biomass having low energy density. In this paper, steam exploded biomass pellets (Black pellets) and unpretreated biomass pellets (Gray pellets) were gasified with air and steam at an updraft HTAG (High Temperature Agent Gasification) unit.

Decomposition characteristics of pellets were first analyzed with TGA (thermo gravimetric analysis). Early decomposition of hemicellulose and cellulose were seen with Black pellets around 241 °C and 367 °C respectively. Introducing CO_2 led comparatively high mass loss rate with Black pellets.

Gasification of Black pellets resulted in syngas with high CO and hydrocarbon contents while Gasification of Gray pellets resulted in high H_2 content of syngas. LHV (lower heating value) of syngas was high around 7.3 MJ/Nm^3 and 10.6 MJ/Nm^3 with air gasification and steam gasification respectively. Even with significantly low syngas temperature with gasification of Black pellets, only slightly high total tar content was seen compared to that of Gray pellets gasification. Phenolic compounds dominated the tar composition.

In general, steam gasification of Black pellets seems to be more feasible if syngas with high energy value is desired. If higher H_2 yield is preferred, gasification of unpretreated pellets likely to be more attractive.

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1. Introduction

With the EU targets of reducing GHG (greenhouse gases) emissions and increasing the share of renewable energy sources in the energy mix, use of biomass as an energy source is in growing concern. However, from an exergetic point of view, highly oxygenated nature of biomass is a barrier for effective use as a fuel [1]. As a result, pretreatment technologies have been developed for better use of biomass in energy applications. Such pretreatment technologies reduce non-uniformity and enhance energy density and also improve some mechanical properties such as hardness, grindability and hydrophobicity of biomass fuel. Most commonly used pretreatment technologies are steam explosion, hydrothermal carbonization and torrefaction.

When considering studies on pretreated biomass, studies on combustion [2–7] or gasification [6,8–10] of torrefied biomass are much common. Similarly, hydrothermal carbonized biomass combustion [11–13] or gasification [14,15] are also increasingly in practice. Main focus of studies on steam explosion pretreatment of biomass is on ultimate use as producing ethanol [16–20]. Even though studies on pyrolysis [21–23] and combustion [24,25] behaviour of steam exploded material also can be found in the literature, such studies on gasification is lacking up to date. Real thermal application of steam exploded biomass is really lacking.

Steam explosion involves heating biomass under high pressure saturated steam and sudden release of pressure assuring explosive decompression resulting dark brown coloured product. Temperature (170–250 °C), pressure (1.2–1.7 MPa) and residence time (10 s

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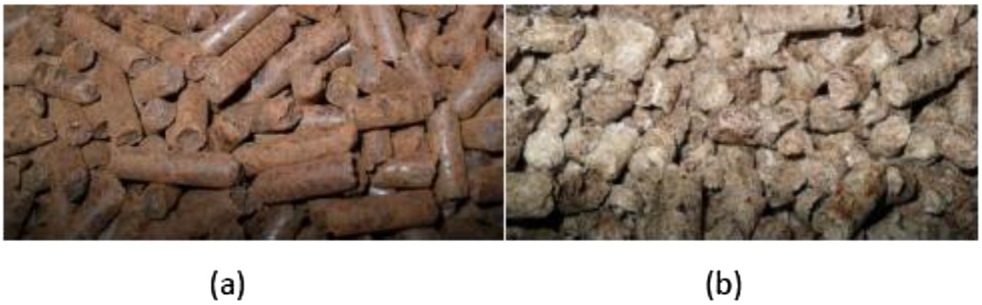

Fig. 1. a. Black pellets b. Gray pellets.

– 10 min) varies depending on required severity of the process. Releasing hemicellulose in to solution and alteration of lignin structures are the main structural changes reported [26–28].

It is reported that energy demand for production of unpretreated pellets and steam exploded pellets are 4.83 MJ/kg and 7–8 MJ/kg (depending on the severity of pretreatment) respectively [29]. Although 45%–65% extra energy is demanded for steam exploded pellets, the quality of pellets is improved in terms of mechanical strength, grindability, energy density and hydrophobicity which are favourable in post processing, transportation and storage. It is reported that biomass feedstock supply logistic cost is around 30–50% of bioenergy production cost [30] providing pretreatment is beneficial for better economy. Further, considering post processing, hydrophobic nature of steam exploded biomass make possibility to inexpensive mechanical dewatering compared to heat drying. It is reported fivefold reduction of drying energy demand after steam explosion pretreatment [25]. Therefore, above mentioned energy demand for pretreatment would be much lower if mechanical dewatering was applied. Further, high durability minimize dusting and reduce material losses while handling and transportation and reduce safety issues related to dust explosion. Energy demand for grinding (while pellet production) also has reportedly reduced by 5–17% due to steam explosion pretreatment [29].

Economy is one of the most important factors that should be considered when it comes to alternative energy sources. The cost of a plant depends on the scale of the plant. When the scale is getting bigger, the cost will become lower. Up to date no economic analysis was found for thermal application of steam explosion process. But, basic economy of the process can be identified from mass and energy balance data. The reported reduction of drying energy demand [25] and reduction of grinding energy demand [29] are some cost benefits expected with pretreatment.

Less alkali content of steam exploded biomass result in low slagging and fouling tendency [31,32]. Stable combustion [33] and similar gaseous emissions compared to other biomass are also reported [31]. Further, low inorganic content reduce fine particulate emission [31]. Less heavy metal content also result in low particulate emission and better ash quality [32]. Considering these facts along with high energy content, steam explosion pretreatment is beneficial in any thermal application including combustion and gasification.

However, it is clear that lack of data on the effect of biomass pretreatment on its gasification process, especial in a pilot scale. Extending the path of our previous researches which focused on steam pretreatment of Salix [32] and its pyrolysis characteristics [21], with above mentioned promising features, we forwarded our attempt to a practical thermal application of pellets produced from steam exploded biomass.

Some researchers claim that even though some pretreatment techniques such as solvent based or ionic liquid based lignocellulose fractionation reduce the crystallinity by disrupting highly ordered hydrogen bonds in crystalline cellulose fibres, dilute acid or steam pretreatment increase the crystallinity due to removal of amorphous fractions such as hemicellulose [34]. Some other researchers [21,24] also found that steam explosion result in increase of crystallinity of biomass. According to a recent study [35] increased crystallinity may cause heat diffusion limitations due to highly ordered crystalline region may act as a barrier to heat diffusion. We expect that these heat transfer limitations may be minimized by using high temperature agent as gasifying medium.

Objective of this work is to evaluate the effect of steam explosion of biomass on its gasification behaviour. Firstly, TGA (thermo gravimetric analysis) study of the steam exploded biomass (Black pellets) was performed, including pyrolysis behaviour and char gasification. Further on, a pilot updraft gasifier with high preheated gasification agent (air and steam) was used to evaluate the effect gasification performance of the Black pellets. Typical unpretreated biomass (Gray pellets) were also used as the reference. However, the aim of this study is not to compare Black pellets with Gray pellets but to study the performance of Black pellets gasification.

2. Experimental

2.1. Feedstock materials

Two types of pellets were used in the experiment; Black pellets and Gray pellets (Fig. 1).

Black pellets were produced and supplied by Zilkha Biomass Energy, Texas, U.S. These pellets are based on 75% soft wood and 25% hard wood, pretreated with steam explosion. The production

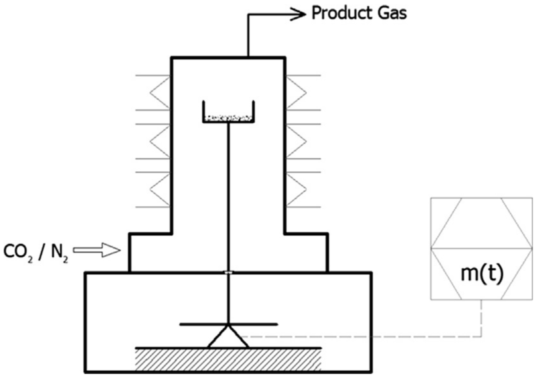

Fig. 2. Schematic diagram of laboratory thermo gravimetric analyzer.

Table 1
Operating conditions.

Run	Biomass type	Biomass feed rate (Kg/h)	Air flow rate (m^3/h)	Steam flow rate (Kg/h)
Air gasification	Black pellets	70	80	–
(ER ≈ 0.2)	Gray pellets	60	75	
Steam gasification	Black pellets	50	10–20	60
(S/B ≈ 1.2)	Gray pellets	50		60

process mainly consist of milling, steam pretreatment, drying and pelletizing. In steam pretreatment, biomass is heated by high pressure saturated steam and the pressure is then suddenly released so that explosive decompression happens.

Gray pellets were produced and supplied by Boson Energy S.A., Luxembourg. Those are based on woody based roadside scrub cuts without thermochemical pretreatment. The only treatment undergone is milling, drying and pelletizing.

Proximate analysis, ultimate analysis, heating value and ash fusion characteristics of both pellet types were measured in an external laboratory and will be discussed in Section 3.1.

2.2. Thermo gravimetric analysis experiment

2.2.1. TGA apparatus

A laboratory thermo gravimetric analyzer (TG 209 F1 Iris, Netsch, Germany) at atmospheric pressure was used to evaluate the decomposition characteristics of two biomass types. A schematic of the system is presented in Fig. 2.

The biomass sample is placed in a ceramic crucible surrounded by a high temperature oven. Both inert and oxidizing atmospheres with variable CO_2 concentrations can be used in this system. The sample is connected to a balance system with a resolution of 0.1 µg. Typically, sample mass of 2 mg is used in the experiments to avoid transfer limitations. The system can be operated up to sample temperatures of 1000 °C.

2.2.2. Experimentation

The pellets were ground and then mixed to homogenize the material. The prepared samples were pyrolyzed under an N_2 atmosphere with a constant heating rate of 30 °C/min from 30 °C to 1000 °C, followed by a 15-min holding time. All the volatile matter assumed to be removed by then.

The remaining sample was cooled to 900 °C at a rate of 30 °C/min, followed by a 15-min holding time. The sample was then gasified in a N_2/CO_2 atmosphere at 900 °C with 10 vol. % CO_2 until constant final weight was observed.

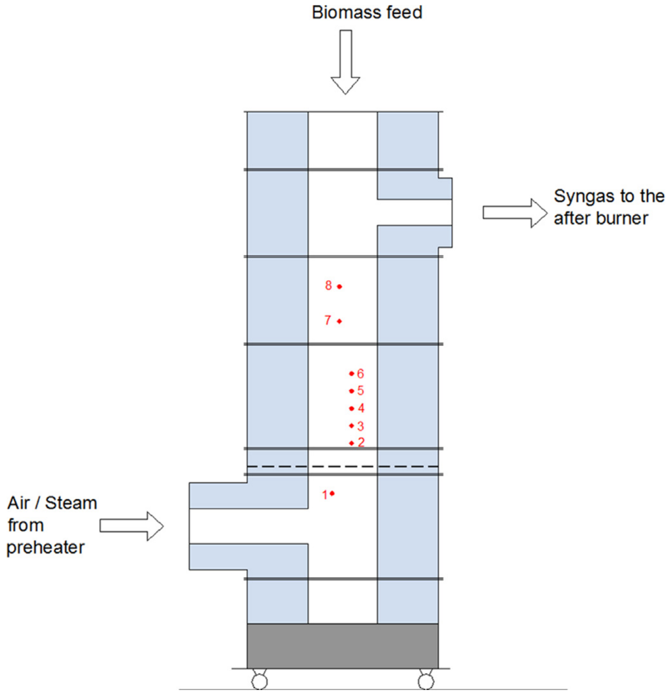

Fig. 4. Cross section of the gasifier with temperature measuring points.

2.2.3. Measurement

The temperature of the sample and the mass of the sample were measured and recorded with respect to time.

2.2.4. Data analysis

Below definitions were used in the data analysis.

DTG (derivative thermo gravimetry) or the first derivative of the residual mass with respect to temperature for the pyrolysis period is defined as,

$$\mathrm{DTG} = -\frac{d\alpha}{dT}$$

Where the residual mass is defined as,

$$\alpha = \frac{\mathrm{Mass}}{\mathrm{Initial\ mass}}$$

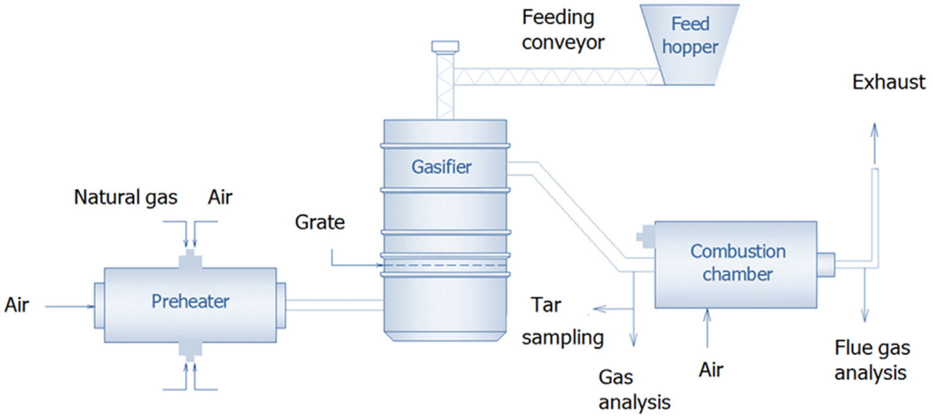

Fig. 3. HTAG system.

2.3. Gasification experiment

2.3.1. Gasifier system

A pilot scale updraft HTAG (High Temperature Agent Gasifier) was used in this study. Use of preheated air/steam as the gasifying medium is the specific feature of HTAG system. The preheated oxidizer supplies additional energy to the gasification process, which enhances the thermal decomposition of the biomass feedstock and increases the product gas yield, gas composition, heating value and cold gas efficiency while reducing the tar content [36]. The unit consists of a feed gas preheater, an updraft gasifier, a fuel feeding system and a syngas post combustion unit (Fig. 3).

A screw conveyor transports the biomass pellets stored in the feed tank to the approximately 3 m high updraft gasifier with internal diameter of 0.4 m. The pre-heater supplies hot air to the gasifier at the side of the bottom section below the grate. The grate is perforated and made from Kanthal steel. This specific steel allows high temperature operation. A boiler supplies steam if steam gasification is to be performed. The biomass and produced hot gases flow countercurrent. The syngas flows upward and leaves the gasifier at the side of the top section. The remaining small particles pass through the grate and collected in the ash box. The post combustion chamber burns out the produced syngas.

2.3.2. Experimentation

Prior to the experiment, pre-calibration of the feeder was done for each type of biomass pellet. Preheating of the gasifier took almost one day. Once the temperature of the gasifier reached the desired value (around 1000 °C in this case), frequency of the feeder was adjusted to fix the feed rate required.

For each pellet type, experiments were conducted with and without steam in the gasifying medium. For air gasification experiments, the ER (equivalence ratio) was kept nearly 0.2 in each case. For steam gasification, steam to biomass ratio was kept around 1.2. A small portion of air was also introduced for each case of steam gasification. Table 1 summarizes the experimental conditions used in each run.

2.3.3. Measurement

Eight type-S thermocouples located along the reactor hight (see Fig. 4) were used to measure the vertical temperature distribution of the gasifier. A data acquisition system connected to a computer was used to record these temperatures at every one minute interval. It was assumed that the horizontal temperature gradient inside the gasifier is not much significant due to the scale of this reactor.

Four digital manometers were used to measure the pressure at different locations along the gasifier to calculate the pressure drop over the fuel bed. The values are recorded in every five minutes. For safety reasons, a negative pressure was ensured at the gasifier top.

GC (Gas chromatograph) was used to measure the dry syngas composition at every three minutes. Water traps ensured the cooling of syngas and dissolution of water soluble tar contained in the syngas, prior to injection to the GC.

SPA (Solid phase adsorption) method was used to tar sampling and analysis. In this method, 100 ml syngas sample was collected to a syringe so that later tar composition analysis is possible. The analysis was done in an external laboratory.

Table 2
Fuel characteristics.

Property	Black pellets	Gray pellets
Proximate analysis		
Moisture content at 105 °C	4.2%	9.8%
Volatile matter (dry)	76.8%	81.2%
Fixed carbon (dry)	22.3%	16.9%
Ash cont. at 550 °C (dry)	0.9%	1.9%
Ultimate analysis (dry basis)		
Carbon C	52.6%	49.4%
Hydrogen H	5.8%	5.9%
Nitrogen N	<0.1%	0.17%
Oxygen O	40.6%	42.6%
Energy content (LHV as received) [MJ/kg]	19.3	16.6
Physical properties of pellet		
Colour	Dark brown	Brown
Resistant to water	High (Hydrophobic)	Low
Durability	High	Low
Diameter [mm]	6	8
Mean length [mm]	17	14
Bulk density [kg/m^3]	740	603
Ash fusion temperatures (oxidizing conditions)		
Shrinking temperature, ST [°C]	1050	1050
Deformation temperature, DT [°C]	1480	1190
Hemisphere temperature, HT [°C]	1490	1210
Flow temperature, FT [°C]	1500	1230

Overall N balance was used to calculate the syngas flow rate of each run. Negative pressure maintained at the top of the gasifier creates the risk of air infiltration to the system through the biomass feeding line. To compensate this error, a correction method was applied when applying N balance. First, the volumetric flow rate of N-free gas stream was calculated by applying C balance assuming negligible C content in the ash. Input N_2 flow rate was then directly added to the volumetric flow rate of N-free gas calculated, to get the total syngas flow rate.

2.3.4. Data analysis

For analysis, a time interval of 20 min was selected for each run based on steady temperature and gas compositions. The average value of each measurement was then taken for the analysis.

The below definitions were used in the data analysis.

$$\text{ER} = \frac{\text{Actual O}_2\text{ mols supplied per one mol of fuel}}{\text{Stoicheometric O}_2\text{ mols required per one mol of fuel for combustion}}$$

$$\text{LHV of syngas} = \sum(\text{LHV of gas species} * \text{molar fraction of gas species in syngas})$$

$$\text{Syngas Yield} = \frac{\text{Syngas flow rate}}{\text{Fuel consumption rate}}$$

$$\text{Energy Yield} = \text{LHV of syngas} * \text{Syngas Yield}$$

$$\text{Cold Gas Efficiency} = \frac{\text{LHV of syngas}}{\text{LHV of fuel}} * \text{Syngas Yield}$$

$$\text{Tar Yield} = \text{Tar content in syngas} * \text{Syngas yield}$$

3. Results and discussion

3.1. *Characterization of feedstock*

Proximate analysis, ultimate analysis, physical properties, energy content and ash fusion characteristics of two pellet types are presented in Table 2 and discussed in the following subsections.

3.1.1. *Proximate analysis*

When considering the proximate analysis of two pellet types, low volatile matter content is observed with Black pellets. The volatile matter content relates to the hemicellulose content because hemicellulose has a branched structure which is easy to volatile. Then, the less volatile matter content in Black pellets is partly due to the less hemicellulose content of raw biomass which is dominated by the soft wood and also possibly due to the loss of hemicellulose while pretreatment.

Further, with the less hemicellulose content, the lignin content of Black pellets should be high and therefore it results in a higher fixed carbon content as seen.

While pretreatment, the biomass undergoes a destruction of lignocelluloses structure and this results in release of mineral matter contained in the original biomass to the liquid phase [32]. This can be the reason for having less ash content of the pretreated sample.

3.1.2. *Ultimate analysis*

Based on the ultimate analysis, the atomic ratios of both pellet types and the raw biomass species are plotted in the Van Krevelan diagram as seen in Fig. 5.

In the diagram, the composition of mixed wood represents the raw biomass for Black pellets and it was roughly calculated from 75% of soft wood and 25% of hard wood. For Gray pellets, the raw biomass composition would be the same as Gray pellets itself, since it has not undergone any thermochemical pretreatment, but only physical treatment.

At this point, it is clear that even though the both wood bases have similar H/C ratios, Gray pellets (and obviously its raw biomass) seems to have more O (or O/C). This is also due to the raw biomass for Black pellets dominate soft wood which has less hemicellulose content and thus less O. However, the significant reduction of both H/C and O/C ratios can be seen with Black pellets due to the steam explosion pretreatment.

3.1.3. *Physical properties*

An important physical property observed with the steam exploded pellets is hydrophobicity. This is also a result of the less hemicellulose content which has more hydroxyl groups which shows a higher affinity to water. Hydrophobicity is a positive factor not only for the transportation and storage but also it creates the possibility to mechanical dewatering which is less expensive than heat drying.

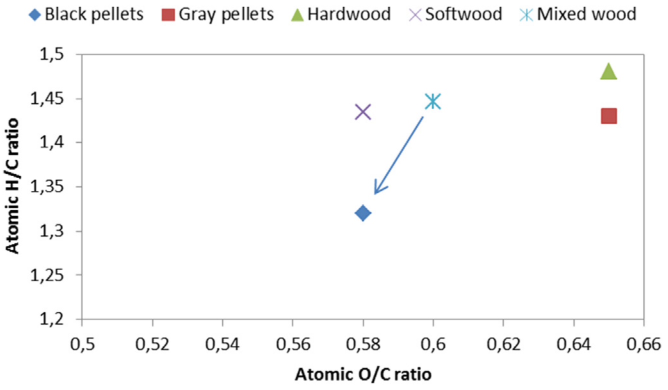

Fig. 5. Van Krevelan diagram of raw biomass, Black pellets and Gray pellets.

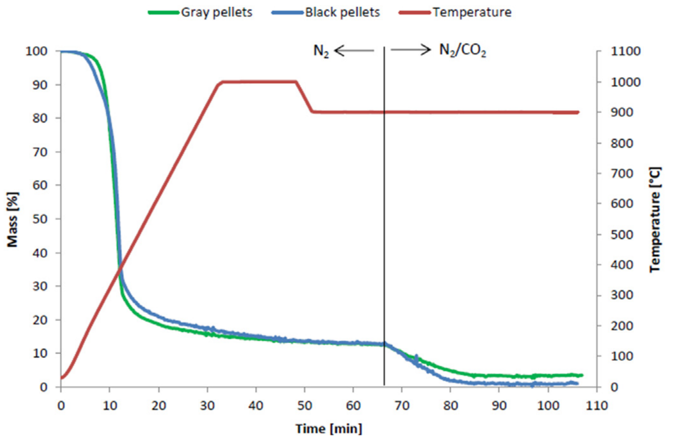

Fig. 6. Mass loss curves obtained with TGA for Black pellets and Gray pellets.

Higher durability was also observed with Black pellets, which minimizes the dusting and reduces the material losses while handling and transportation. This can also reduce the safety issues related to dust explosion.

One reason for the high bulk density seen with Black pellets is the small diameter of Black pellets used in this experiments which is 6 mm compared to 8 mm Gray pellets. It is also reported that severe treatment of biomass has resulted in more fines and hence results in a higher pellet density [32]. Therefore, the high bulk density can be expected even with a same pellet size.

3.1.4. *Energy content*

Generally, C and H give a positive effect on the heating value of biomass while O, N and ash give a negative effect. High C and less O and ash could be the reason for having a high LHV (lower heating value) of Black pellets in which part of this upgrading of LHV should be attributed to the raw biomass of Black pellets.

Both the facts high heating value and high bulk density result in increase of the energy density which is an important factor related to transportation and storage. The energy density of Black pellets is 14.3 GJ/m^3 and it is 10 GJ/m^3 for Gray pellets. However, it should be noted that a part of improvement of energy density of Black pellets can be due to its small pellet size and less O contained raw biomass. High energy density results in the reactor to be more compact due to need of a less volume.

3.1.5. *Ash fusion characteristics*

High ash fusion temperature seen with Black pellets can be related to the low alkali metal content expected with steam explosion pretreatment. In order to avoid slagging, the gasifier should be operated below the ash deformation temperatures ie. 1190 °C with Gray pellets and 1480 °C with Black pellets. This high temperature limit is a plus point for the high temperature gasification of Black pellets. Further, steam gasification also minimizes the ash agglomeration by lowering the reactor temperature due to the endothermic steam carbon reactions as reported [37].

3.2. Characterization by TGA

3.2.1. Mass loss

The decomposition behaviour of both pellet types were studied based on the thermo gravimetric residual mass curve presented in Fig. 6.

According to Fig. 6, for both pellet types, approximately 87% of the mass is lost in the first stage, which was carried out under an inert atmosphere (pyrolysis stage). After the completion of this mass loss, the introduction of CO_2 yields another mass loss region, as shown in the figure. This mass loss, which is approximately 12% and 10% of the total mass loss for Black pellets and Gray pellets respectively, is attributed to the gasification of residual C with CO_2. Nearly 1% and 3% of the mass respectively remained at the end can be identified as ash.

It can be noted that the values of proximate composition obtained from this TGA method is different from those values obtained from ASTM method in Table 2. This difference can basically be due to two factors; the different heating rates applied and the different oxidizing atmospheres. The typical oxidizer used in the ASTM method is O_2 while CO_2 was used in the TGA.

3.2.2. Derivative thermo gravimetry

The constant heating rate period in the pyrolysis stage was further studied using the DTG plot given in Fig. 7, which is the first derivative of the residual mass curve.

There are several major differences seen with DTG plot of Black pellets compared to that of Gray pellets and reported typical biomass. In most of the cases with biomass, the hemicellulose peak is merged in the cellulose peak and observed as an asymmetrical shaped peak which is also seen with DTG plot of Gray pellets. Due to the steam explosion pretreatment, a part of hemicellulose in the raw biomass is decomposed and released to the solution while the remaining hemicellulose is depolymerized. Then, an early stage peak from 150 to 290 °C with a maximum decomposition rate of 0.13%/°C around 241 °C can be seen attached to the major peak from 290 to 400 °C. This can be explained as due to de-polymerization of the remaining hemicellulose components, the peak has shifted to a lower temperature which is otherwise merged in the cellulose peak. Previous researchers [21] also observed an overall high intensity of decomposition in the region before cellulose peak with steam exploded Salix which is also approximately in the same temperature range as observed in this study. Further, they have observed a peak around 150 °C attributed to crosslinking of liquefied D-xylose. But, this peak has disappeared with very severe pretreatment conditions in their study due to destruction of D-xylose in to small molecules. In this study, we do not see a clear peak around 150 °C and also we observe a more clear peak attributed to hemicellulose which is attached to the cellulose peak. This may be due to more severe pretreatment undergone.

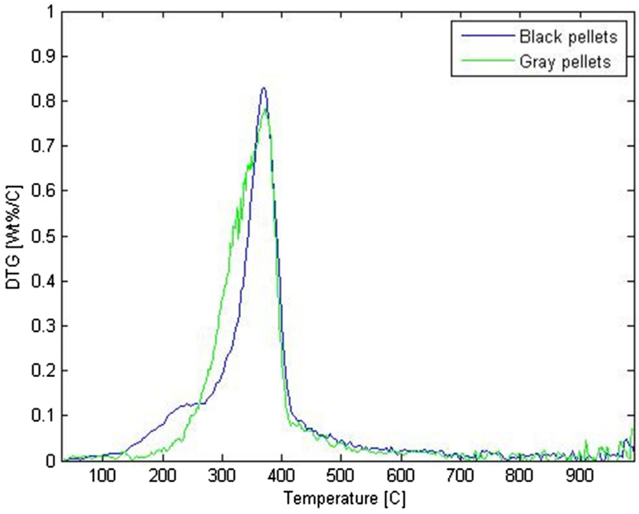

Fig. 7. DTG plots for Black pellets and Gray pellets.

The cellulose peak shows a maximum decomposition at 367 °C. This peak temperature is slightly lower than that of Gray pellets which is around 372 °C and also compared to typical biomass which is around 384 °C [21] and 381 °C [23] with Salix (Willow) which is a hard wood and 391 °C with Spruce [23] which is a soft wood. Hard wood decomposes earlier than soft wood due to more hemicellulose present. Therefore, more prominent peak shift could be seen if the reference fuel was the raw biomass used for Black pellet production (which dominates soft wood). This kind of low thermal stability of cellulose due to the steam explosion pretreatment has also been observed by some other researchers [21–24]. The maximum decomposition rate of cellulose is also higher with Black pellets (0.83%/°C) compared to Gray pellets (0.79%/°C). This low thermal stability and high decomposition rate of cellulose can be explained by separation of the hemicellulose peak from the cellulose peak. When hemicellulose and cellulose both decompose in a more overlapped temperature range as in typical biomass, melting hemicellulose in the cellulose surface will suppress the cellulose decomposition and cellulose will decompose at higher temperature. But, separate peaks means most of the hemicellulose is already decomposed when it comes to cellulose decomposition temperature range and it will facilitate an easy decomposition of cellulose and hence at comparatively lower temperature. Further, with severe pretreatment, depolymerization of cellulose is also reported [22] and it can be another reason for having low thermal stability of cellulose.

Beyond the cellulose peak above 400 °C, it can be seen a gradual decomposition region with small peaks in both DTG curves which can be attributed to lignin decomposition. At the beginning of this region, slightly higher intensity is seen with Black pellets. Further, even though it could not be clearly seen in this study, a low lignin decomposition temperature has been observed by some researchers [21,24] with steam exploded biomass. This might be a result of early cellulose degradation. Adsorption of the cellulose pyrolysate on the lignin or char surface can delay the decomposition of the lignin in typical biomass and with early cellulose degradation, this inhibition is less. Further, the reported change of lignin structure also may have influence.

Therefore, compared to Gray pellets, early thermal degradation of all the three basic components of Black pellets can be expected in the pyrolysis stage of the gasifier. However, the actual degradation temperatures in the fixed bed may be considerably higher than that is observed in TGA because of heat transfer limitations when it comes to pellet form along with the high crystalline structure of the steam exploded biomass. However, this limitation can be minimized with high temperature operation.

3.2.3. Char gasification

If the period of char gasification is considered, the mass loss rate of Black pellets is higher than that of Gray pellets as seen in the residual mass curve (Fig. 6). These rates were calculated as 0.88%/min and 0.55%/min respectively with Black pellets and Gray pellets. This can be due to high C content of Black pellets which effectively forward Boudouard reaction towards CO production. However, the reaction rate that can be obtained with real gasification application can be lower due to less surface area available for reaction due to big particle size when it comes to pellet form.

It is also reported that CH$_3$ radicals formed from lignin derived methoxy groups accept H radicals from cellulose derived primary volatiles [38]. They have also claimed that, this type of abstract of H by lignin derived radicals enhance the gasification of cellulose derived primary volatiles. Then, the presence of more lignin (particularly methoxy group of lignin) in Black pellets may have a positive effective in gasification of cellulose fraction in the real gasifier since pyrolysis and gasification altogether happening in the same time.

3.3. *Gasification in updraft HTAG*

3.3.1. *Temperature distribution*

The vertical temperature profile along the gasifier height for each case of experiment is given in Fig. 8.

As seen in Fig. 8, the temperature is highest at the bottom of the bed, and gradually decreases along the bed height. It is because all the sensible heat was supplied to the gasifier by the high temperature agent that was supplied from the bottom of the gasifier. However, the typical peak temperature expected at the combustion zone is not seen here possibly due to a thin combustion zone and hence at the second temperature measurement point, the reduction process has already started. Therefore, temperature profiles basically features two regions; A significant temperature drop in the bed zone and an almost flat temperature profile in the gas phase.

The high temperature drop observed in the bed area is mainly due to the endothermic Boudouard reaction. Gasification of Black pellets shows large temperature drop compared to the gasification of Gray pellets due to high C content of the fuel. In contrast, better temperature uniformity within the gasifier is seen with Gray pellets gasification due to less C and high volatile content of Gray pellets. Both steam gasification cases show low temperature compared to respective air gasification cases except in the bed zone of Black pellets steam gasification case. These features can be related to the extent of reactions happening in each zone and will be further explained with syngas composition later in the Section 3.3.3.

It is worth to note that the heat diffusion limitations are considered minimum in high temperature gasification. The temperature of the bed area was always above 800 °C for gasification of Gray pellets. Further, due to less mechanical strength of Gray pellets, disintegration of Gray pellets is assumed high while gasifying. These facts ensure better heat diffusion even though the pellet diameter of Gray pellets is high.

3.3.2. *Bed pressure drop*

The biomass bed height inside the gasifier and the bed pressure drop of each experimental case are summarized in Table 3.

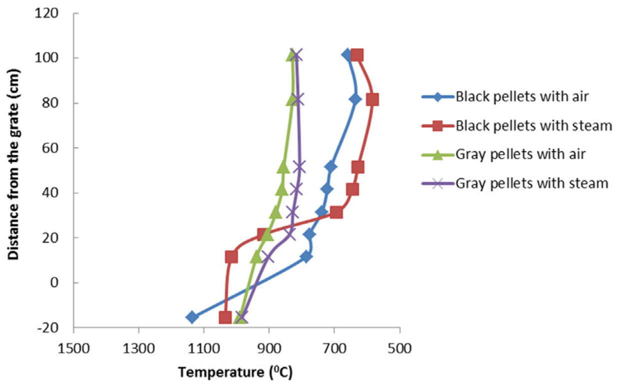

Fig. 8. Temperature profile along the gasifier height.

Basically, the pressure drop through a gasifier bed is the sum of pressure drop through the particle bed and the pressure drop through the grate. Since the grate resistance is minimum in this study due to the high grate opening area, the pressure drop through the particle bed dominates the total pressure drop as discussed in our previous publication [39].

When considering the bed heights, if the rate of biomass feeding is greater than the rate of gasification, the bed height will increase. However, when considering biomass feeding rates used referring to Table 1, the gasification cases with Black pellets always had equal or higher biomass feed rate than the cases with Gray pellets. Then, one reason for having a larger bed height with gasification of Gray pellets can be, low bulk density of Gray pellets. But, since the difference of bulk densities of two pellet types is not that much high (refer Table 2), slow gasification rate (hence development of bed) of the gasification cases with Gray pellets compared to that of Black pellets may be another reason for this. This fact aligns with the TGA results also. As a result, even with small particle size of Black pellets (which should increase the pressure drop), low pressure drop is seen with gasification of Black pellets due to low fuel bed.

3.3.3. *Syngas composition*

Fig. 9 shows the compositions and characteristic ratios of syngas from gasification of Black pellets and Gray pellets with highly preheated air.

Higher CO content in syngas obtained with gasification of Black pellets and high H$_2$ content of syngas obtained with gasification of Gray pellets are seen. This can be explained by difference of H/C ratio of two samples discussed in section 3.1. The CO and H$_2$ content of syngas can be mainly a result of H/C ratio of two pellet types rather than O/C ratio. Then, since H/C ratio of raw biomass for Black pellets and the Gray pellets are similar (even though O/C ratios are quite different), high CO content and less H$_2$ content of syngas obtained by gasification of Black pellets can be due to reduced H/C ratio after pretreatment.

Black pellets gasification with air yield very high CO/CO$_2$ ratio in syngas which is around 3.3 compared to that of the case with Gray pellets which is around 1.4. Then, it seems that the Boudouard reaction is more effective with Black pellets gasification. This was seen in TGA results also with high rate of char gasification of Black pellets. Further, this effect is seen in temperature profiles which shows high temperature drop in the cases with Black pellets as discussed earlier in the Section 3.3.1.

Due to easy disintegration of Gray pellets, the exposed surface area of C available for reacting with CO$_2$ should be higher compared to Black pellets even though the original diameter is higher. Even with this fact, Black pellets show much better performance in gasification.

Higher hydrocarbon content and high CH$_4$/H$_2$ ratio in syngas obtained with gasification of Black pellets can be explained by low syngas temperature which does not dominate hydrocarbon cracking reactions.

High CH$_4$ content of syngas can be further expected by high lignin content of Black pellets which contains methoxy ($-$O$-$CH$_3$) group which results in formation of CH$_4$ while pyrolysis. However,

Table 3
Bed height and pressure drop.

Run	Biomass type	Bed height (mm)	Pressure drop (mbar)
Air gasification (ER ≈ 0.2)	Black pellets	220	4.5
	Gray pellets	550	10
Steam gasification (S/B ≈ 1.2)	Black pellets	220	5.2
	Gray pellets	600	12.9

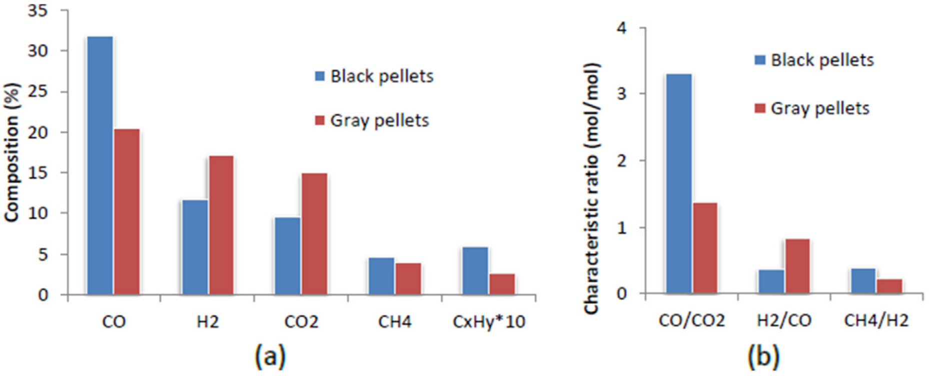

Fig. 9. Air gasification a. Gas compositions b. Characteristic ratios.

it is reported that during steam explosion pretreatment, cleavage of methoxy group and $-CH_2-OH$ group both can happen [40]. Then, if it can be selectively reduce cleavage of methoxy group during pretreatment, it will be beneficial in gasification process for high CH_4 yield in syngas. Since bond energy of C—O bond is higher than a C—C bond, this might be possible with optimized pretreatment temperature.

Fig. 10 shows the compositions and characteristic ratios of syngas from gasification of Black pellets and Gray pellets with high preheated steam.

Steam gasification also shows the same trends as air gasification for syngas composition except for CH_4.

When it comes to steam gasification, the water-gas shift reaction is one of the main reactions that is to be considered. However, the water-gas shift reaction seems not dominate in the case of steam gasification of Black pellets since H_2/CO ratio of the syngas does not show a significant improvement compared to the air gasification case. This may be due to occurrence of the Boudouard reaction at high bed temperature (CO/CO_2 ratio of 3.7 can be seen) resulting comparatively a low temperature when it comes to gas phase as seen in Fig. 8 which is not favourable for water gas shift reaction. The water gas shift reaction is reportedly more effective in the temperature range of 730–830 °C [41].

Drop of CH_4/H_2 ratio in the syngas obtained with the steam gasification of Black pellets compared to that of air gasification seems to justify the hydrocarbon reforming reactions with available steam.

With steam gasification of Gray pellets, high H_2/CO ratio and low CO/CO_2 ratio of syngas can be seen as expected with the dominant water gas shift reaction due to higher gas phase temperature. The effect of the Boudouard reaction has overcome by the water gas shift reaction consuming more CO. Higher hydrocarbon content of the syngas implies that the steam reforming reactions are also not much significant in this case. This fact is further explained by no drop of CH_4/H_2 ratio of the syngas compared to the air gasification case.

3.3.4. LHV, syngas yield, energy yield and cold gas efficiency

Table 4 shows the LHV of syngas, syngas yield, energy yield of syngas and cold gas efficiency of the tested cases.

With the case of black pellets gasification, the main contribution to the heating value of syngas comes from CO and hydrocarbon contents of syngas which are considerably higher than that with Gray pellets gasification because of the dominance of Boudouard reaction and low gas phase temperature respectively as discussed above. On the other hand, the contribution to the heating value of syngas obtained from the gasification of Gray pellets dominates by CO and specially H_2 content of syngas. More hydrocarbon content in the syngas yields higher LHV of syngas when gasifying Black pellets. Further, due to increased share of combustibles in the syngas and the reduced dilution of syngas with N_2, a higher LHV of the produced syngas can be seen with both cases of steam gasification compared to air gasification.

The syngas yield obtained with the gasification of Black pellets is slightly lower than that obtained with the gasification of Gray pellets. This may be due to the less volatile matter content upon the pyrolysis of Black pellets as seen in the proximate analysis and less thermal cracking reactions seen with gasification of Black pellets.

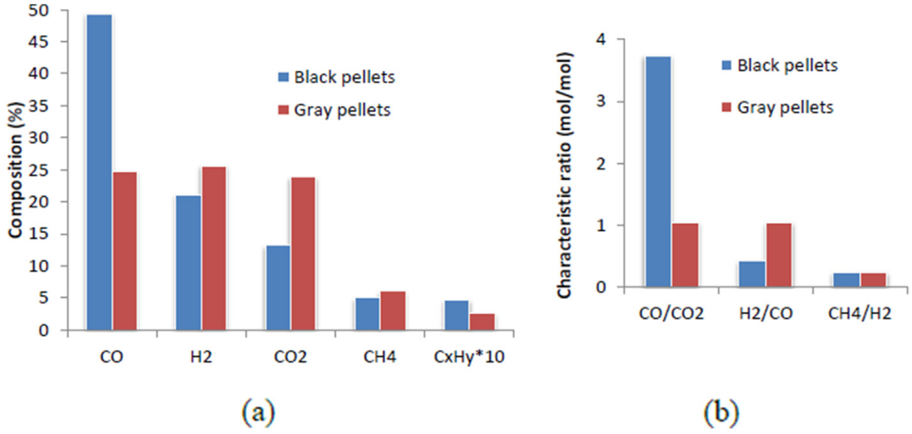

Fig. 10. Steam gasification a. Gas compositions b. Characteristic ratios.

Table 4
LHV, syngas yield, syngas energy yield and cold gas efficiency.

Run	Biomass type	LHV of syngas (MJ/Nm^3)	Syngas yield (Nm^3/kg dry fuel)	Energy yield of syngas (MJ/kg dry fuel)	Cold gas efficiency (%)
Air gasification (ER ≈ 0.2)	Black pellets	7.3	2.0	14.6	75.6
	Gray pellets	6.0	2.1	12.6	75.9
Steam gasification (S/B ≈ 1.2)	Black pellets	10.6	1.4	14.8	76.9
	Gray pellets	8.2	1.5	12.3	74.1

Further, the steam gasification results in a lower syngas yield possibly due to the reduced dilution of syngas with N_2.

When the syngas energy yields obtained by gasification of two pellet types are considered, Black pellets gasification results in a higher energy yield compared to that of Gray pellets due to the high LHV of syngas obtained. However, it seems that the steam gasification does not have much effect on the syngas energy yields obtained with gasification of both pellet types. This is due to the low syngas yield even with the high LHV in steam gasification.

Cold gas efficiency of each case is comparatively high and is in the range of 74–77%. It seems that the cold gas efficiency is not significantly changed with the type of biomass (Black pellets or Gray pellets) or the type of feed gas (air or steam). This can be due to the high temperature operation of HTAG.

3.3.5. *Tar content in syngas*

For more clear comparison of tar composition, the identified tar species of syngas are grouped in to three categories: BTEX (Benzene/Toluene/Ethyl benzene/Xylenes), Phenol and Cresols, PAH (Polycyclic Aromatic Hydrocarbons).

Fig. 11 shows the share of these three categories in tar content and the composition of each category by compound.

For air gasification, PAH category is the most abundant in the tar composition in both Black pellets and Gray pellets gasification. Phenol and Cresols are the least abundant group.

The contribution of BTEX in tar composition is similar for both Black pellets and Gray pellets gasification. However, Benzene dominates the BTEX share of Gray pellets gasification and it is nearly two times the case with Black pellets.

Air gasification of Black pellets show low PAH and high Phenol and Cresols share in the tar composition compared to air gasification of Gray pellets. This is further prominent with steam gasification of Black pellets.

High phenol and cresols content of Black pellets derived tar can be due to high carbon content of Black pellets and its effect on low gas phase temperature. At high temperatures, phenol and cresols convert to PAH such as indene, naphthalenes and other aromatics which we see a higher content with Gray pellets gasification. This type of aromatization of remaining tars at high temperature and favourable production of phenolic compounds with high steam content and low temperature is reported in the literature [42,43].

Further, most abundant PAH produced by gasification of each pellet type are the lighter ones such as Indene and types of Naphthalene.

Table 5 shows the tar content, tar yield and tar dew point of each case of experiment.

Even with significantly low syngas temperature seen with Black pellets gasification, which limits tar thermal cracking reactions, only slightly higher total tar content and tar yield was seen revealing a positive point with Black pellets gasification. This can be due to high lignin content of Black pellets. It was reported that, crosslinking reactions between cellulose and lignin cause less tar during pyrolysis [44].

It is found that, with steam gasification, tar content of syngas has been reduced even though the syngas exit temperature is low.

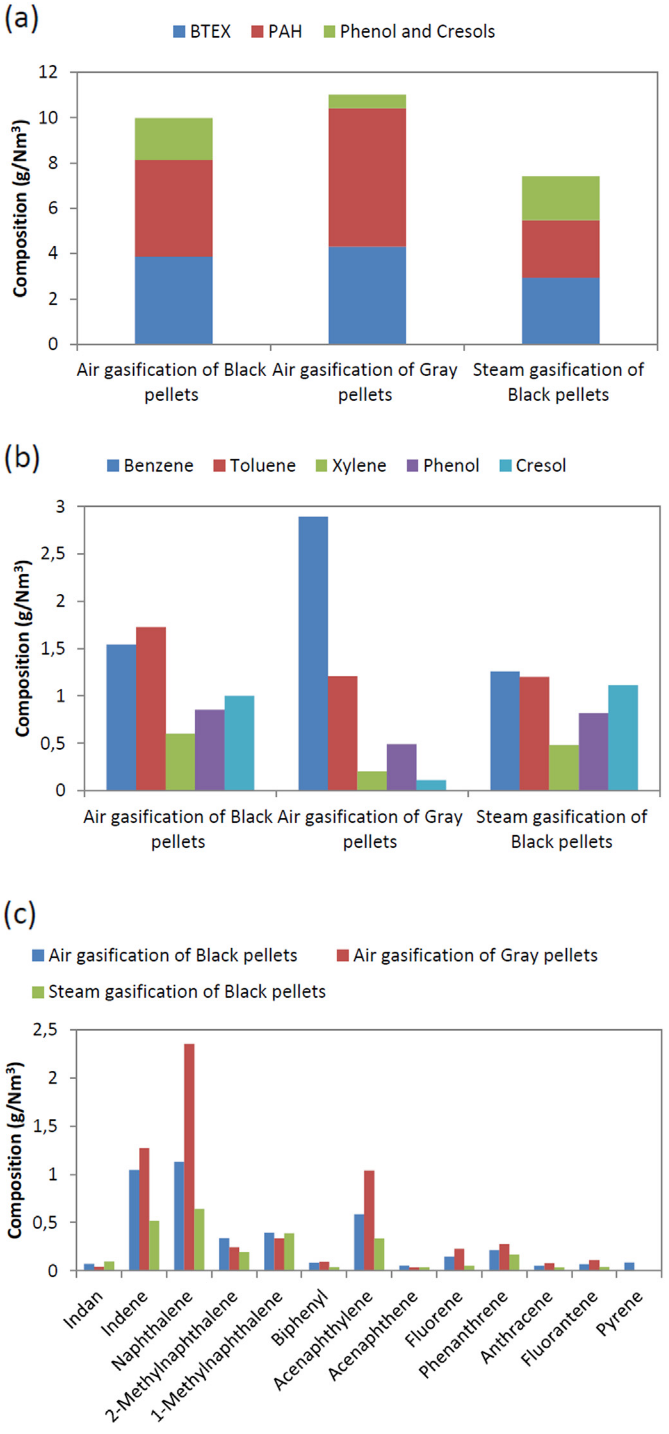

Fig. 11. Tar composition based on identified tar species: a) By category b) BTEX, Phenol and Cresols c) PAH.

Table 5
Tar characteristics.

Parameter	Air gasification of black pellets	Air gasification of gray pellets	Steam gasification of black pellets
Total tar content (g/Nm^3 syngas)	15.4	13.4	11.4
Tar yield (g/kg dry fuel)	30.8	28.1	16.0
Tar dew point (°C)	108	105.4	93.3

Then, in that case, steam reforming of tar has compensated the negative effect on thermal cracking of tar at low syngas temperature in to some extent.

Since only the gravimetric tar content is not enough to assess the syngas quality, the tar dew point, which is the temperature at which tar condensation begins upon cooling of the syngas is considered. For a single tar compound, the tar dew point can be calculated from the equation [45],

$$22400\frac{C}{M}\frac{T}{273}\frac{1}{P_{\mathrm{sv}}(T)} = 1$$

where the C is the concentration of tar species, M is the molecular weight of tar species and P_{sv} is the saturation vapour pressure at temperature T.

For a mixture of tar compounds, the dew point can be calculated in a similar manner by taking the sum of each contribution. Based on this, the complete dew point model developed by Energy Research Centre of the Netherlands [46] was used to calculate the tar dew points in this study.

The dew points are around 100 °C in all cases. This implies that the tar will not condense in the syngas outlet pipe since syngas outlet temperature is high as much as 600 °C. This was also observed during the experimental process.

Generally PAHs contributes to a high dew point of tar. However, even with high PAH content of tar obtained from air gasification of Gray pellets, slightly low tar dew point was observed compared to Black pellets. This can be due to high share of low boiling point Benzene and Naphthalene respectively in BTEX and PAH categories of tar obtained from gasification of Gray pellets.

4. Conclusions

From the results obtained, following conclusions can be drawn.

Steam explosion pretreatment improves the physical properties and energetic properties of biomass providing positive approach in thermal applications. The high ash fusion temperatures further facilitate high temperature operation which is the main feature of HTAG facility used in this study.

Steam exploded biomass (Black pellets) features an early stage hemicellulose degradation, a low thermal stability of cellulose fraction and a high rate of char gasification in TGA experiment providing preliminary understanding necessary for a real thermal applications.

Gasification of Black pellets in HTAG system results in more diverged temperature profile in the gasifier and less pressure drop of the fuel bed. Further, effective Boudouard reaction and suppressed water-gas shift reaction are features of gasification of Black pellets, resulting more CO but less H_2 in syngas. Furthermore, all the thermal cracking reactions are suppressed and thus result in high LHV of syngas but slightly less syngas yield. The cumulative effect is high syngas energy yield around 15 MJ/kg of dry fuel, irrespective of the gasifying agent. Then, the gasification of Black pellets seems to be more feasible if syngas with high energy value is desired and if higher H_2 yield is preferred, gasification of unpretreated pellets likely to be more attractive which gives more H_2 share in syngas.

As a feature of the HTAG system, the cold gas efficiency is in a comparable range for each case around 74–77% irrespective of the type of biomass (Black pellets or Gray pellets) or the type of feed gas (air or steam).

The tar composition of syngas obtained with Gasification of Black pellets dominates phenolic compounds which even more prominent with steam gasification. This reduced aromatization to produce PAH is a positive factor if carcinogenicity of PAH is considered. Further, a low tar dew point around 100 °C is seen in all gasification cases, which is much below the syngas exit temperature enabling more freedom for downstream processing temperatures.

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